Supporting Information

Contrasting guest binding interaction of cucurbit[7-8]urils with neutral red dye: Controlled exchange of multiple guests

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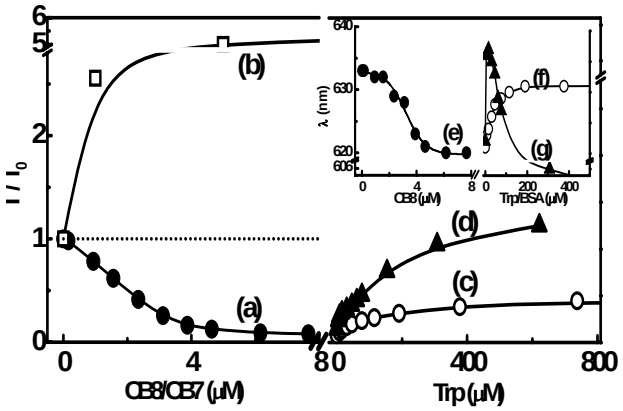


Fig. S1: Relative fluorescence intensity changes recorded for NRH^+-CB8 (**a**) and NRH^+-CB7 (**b**) interaction. (**c**) and (**d**) represent the recovery of fluorescence signal obtained when Tryptophan or BSA was added to the $(NRH^+)_2$**.**CB8 system, respectively. Inset shows the emission wavelength changes during NRH^+-CB8 titration (**e**) and during the titration of $(NRH^+)_2$**.**CB8 with Tryptophan (**f**) or BSA (**g**).

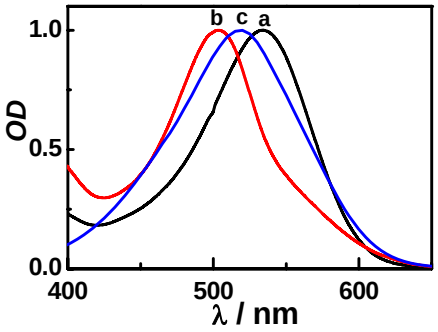


Fig. S2: Absorption spectra of an aqueous solution of NRH^+ without CB8 (a), with CB8 (b). Spectrum (c) represents the absorption spectrum recorded from a concentrated solution of NRH^+ using a 1mm path length, indicating the presence of a dimeric species.

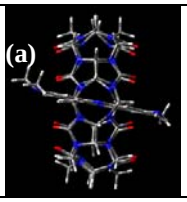
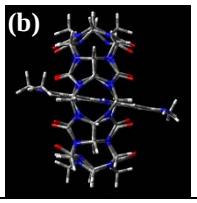
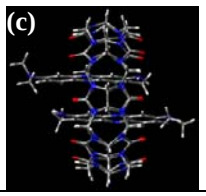
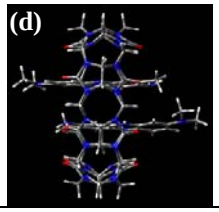
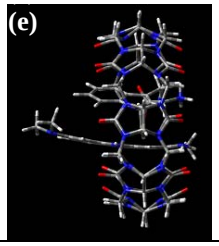
	**1:1 NR:CB8 Complex** NR+CB8 → NR**.**CB8 ΔH_f= -1.23kcal/mole
	**1:1 NRH^+:CB8 Complex** NRH^++CB8 → NRH^+**.**CB8 ΔH_f= -39.9kcal/mole
	**2:1 NR:CB8 Complex** 2NR+CB8 → $(NR)_2$**.**CB8 ΔH_f= +21.64kcal/mole
	**2:1 NRH^+:CB8 Complex** 2NRH^++CB8 → $(NRH^+)_2$**.**CB8 ΔH_f= -9.5kcal/mole
	**1:1:1 NRH^+:CB8: Trp Complex** NRH^++CB8+ Trp → NRH^+**.**CB8**.**Trp ΔH_f= -7.15kcal/mole

Fig. S3: Computationally optimized geometries of various stoichiometric arrangements for neutral red-CB8 interaction (a-d). Structure (e) represents the optimized geometry for the NRH^+.CB8. Trp Complex.

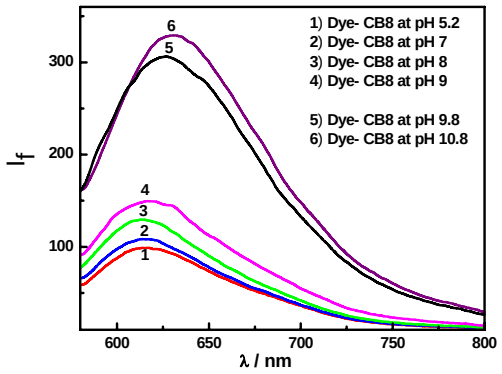


Fig. S4: The fluorescence spectra recorded for the neutral red-CB8 system at different pHs, maintain the excitation parameters the same

Note: 1

The binding curve obtained for NRH^+-CB8-BSA system (Fig.7, inset) were analyzed by the equations according to the following 1:1 interactions

$$CB8.(NRH^+)_2 + BSA \longleftrightarrow NRH^+.CB8.BSA + NRH^+ \quad \textbf{S1}$$

$$NRH^+ + BSA \longleftrightarrow NRH^+.BSA \quad \textbf{S2}$$

Taking $[Dye]_0$ and $[BSA]_0$ as the total concentrations of dye and BSA, respectively, eq. S3 applies for the concentration of free (uncomplexed) dye in equilibrium:

$$[Dye]_{eq} = \{K_{eq}[Dye]_0 - K_{eq}[BSA]_0 - 1 + \sqrt{(K_{eq}[Dye]_0 + K_{eq}[BSA]_0 + 1)^2 - 4K_{eq}^2[Dye]_0[BSA]_0}\} / 2K_{eq} \quad \textbf{S3}$$

Where [Dye] represents the concentration of CB8•$(NRH^+)_2$ complex for Eqn **S1** and NRH^+ for Eqn **S2.**

The fluorescence intensity can therefore be understood as a composite of the fluorescence intensity contributions from the complexed and uncomplexed forms according to eq. S4:

$$I_f = I^0_{Dye} \frac{[Dye]_{eq}}{[Dye]_0} + I^{\infty}_{Dye.BSA} \frac{[Dye.BSA]_{eq}}{[Dye]_0} \quad \textbf{S4}$$

where I^0_{Dye} is the initial fluorescence intensity in the absence of CB8 and $I^{\infty}_{Dye.BSA}$ corresponds to the fluorescence intensity if all the dye molecules in the solution were complexed by BSA. The change in fluorescence intensity (ΔI_f) can be obtained by rearrangement (eq.S5):

$$\Delta I^{\lambda}_f = (1 - \frac{[Dye]_{eq}}{[Dye]_0}(I^{\infty}_{Dye.BSA} - I^0_{Dye}) \quad \textbf{S5}$$

In the fluorescence titrations, we employed the fluorescence intensity as experimental measure. The concentration of (Dye) was kept constant at a particular pH 5 and the concentration of BSA was varied. The binding constants (K) obtained from the nonlinear fittings of the experimental data using Eqn. S5 were $2.5x10^5$ M^{-1} for the CB8•$(NRH^+)_2$ complex with BSA and $3x10^3$ M^{-1} for the NRH^+ with BSA.